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Flame Retarded Poly(lactic acid) Using POSS-Modified Cellulose. 2. Effects of Intumescent Flame Retardant Formulations on Polymer Degradation and Composite Physical Properties

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Abstract

Poly(lactic acid), PLA, was extruded with intumescent flame retardant formulations based on ammonium polyphosphate, APP. Nanofibrillated cellulose fibers (NFC), POSS-modified NFC (PNFC), and pentaerythritol (APP) were used as the additional carbon source. The effects that each additive and their intumescent combinations had on polymer degradation, flammability, crystallization, melt rheology, and tensile properties were systematically examined. APP and PER catalyzed the degradation of PLA during extrusion, which increased the crystallinity of PLA, lowered the viscosity of the melt, reduced the moduli, and decreased the tensile strength of the composite. The POSS moieties on PNFC acted as plasticizers in melt rheology studies, but did not affect the glass transition temperature. PNFC formed a cross-linked network with APP when melt-blended with PLA, which reduced polymer degradation, decreased PLA crystallinity, changed the rheological behavior, and improved composite stiffness. These composites exhibited

the highest viscosities and storage moduli at low frequencies. Higher shear disrupted the network, and the plasticizing effect of PNFC dominated at high frequencies. The PLA composites containing APP and PNFC had the best tensile properties of all the intumescent composites studied. The cross-linked network formed between cellulose, POSS, and PLA helps produce composites with superior flammability, rheological, and mechanical properties relative to other intumescent formulations.

Cellulose, PLA, polyoligomeric silsesquioxane, XRD, DSC, crystallinity, rheology, tensile strength

1. Introduction

Recently, increasing concern about the environment and public health has encouraged the use of materials derived from renewable sources. Because of the versatility and prevalence of polymers in many industries, a considerable amount of research has been conducted on biodegradable polymer substitutes for common petroleum-based polymers.[1, 2] For instance, poly(lactic acid) (PLA), a nontoxic and biodegradable polymer derived from corn and other plants,[3-5] has applications in food packaging,[4] disposable utensils,[6] and medical devices[4, 7] because of its mechanical strength and relatively high melting point.[8, 9] Chemicals have also been added to PLA to counteract its brittleness,[7, 10] limited barrier properties,[11-13] and flammability.[3, 14-17] PLA composites can be used in textiles,[14, 18] casings for electronic devices,[18, 19] and automotive parts,[20] but are subject to strict flammability requirements.

Intumescent flame retardants (IFRs) are one of the most promising additives for reducing the flammability of PLA. Although inorganic compounds[21-23] and nanoparticles[23-27] are also used as flame retardant additives, IFRs are halogen-free and produce less smoke.[9, 28] The Bourbigot group has reviewed many flame retardant studies for PLA and reported that the majority work through the condensed phase mechanism.[18] IFRs consist of an acid source, a carbon or char-forming source, and a blowing agent; together they produce a foamed char barrier that reduces heat and fuel transport.[9, 29] A commonly used IFR is a combination of ammonium polyphosphate (APP) and pentaerythritol (PER). It has been shown to reduce

flammability with little smoke production,[28, 30, 31] However, IFRs, especially those based on polyphosphates, are prone to poor weatherability,[32-36] reduced viscoelasticity,[28, 37-39] and reduced mechanical strength.[40-44]

Recently, investigations into carbohydrate-based replacements for the petroleum-based carbon source, PER, have been carried out in PLA.[6, 16, 39, 45-48] Not only are these materials biodegradable and sustainable, but also many of them are water insoluble and improve mechanical properties, such as stiffness and mechanical strength. Sugars, starch, and lignin have been used to improve the charring and flammability characteristics of intumescent PLA.[6, 16, 45, 47] However, it has been shown that lignin, starch, and starch thermoplastics increase the water sensitivity and degradation rates while lowering the tensile and impact strengths of PLA and intumescent PLA composites.[49-52] The incorporation of ramie fibers and APP into PLA produced composites with higher storage modulus, but decreased mechanical strength at higher loadings of APP.[39] Pack, et al. found that increased compatibility between starch coated with resorcinol di(phenyl phosphate) and a blend of Ecoflex and PLA resulted in significantly higher toughness of the composite, while also achieving a designation of V-0 in UL-94 flammability tests.[53] In most of these studies, it was found that the presence of APP increased acid hydrolysis of the polymer and additives. This could be minimized by microencapsulating the APP with polyurethane.[45, 54] Despite the improved flame retardancy of these composites, the problem of reduced mechanical properties remains.

An IFR additive that may be effective at reducing all of the IFR disadvantages is polyhedral oligomeric silsesquioxane (POSS). It has been shown to reinforce composites while also reducing flammability by forming stable char with a structure that is similar to ceramic.[24, 55-57] This can help form more durable chars, resulting in synergistic effects when used in conjunction with an intumescent flame retardant.[58, 59] One of the advantages of POSS is that organic substituents can be added to the exterior of its cage-like core of Si – O ($\text{SiO}_{1.5}$).[60, 61] Because the substituents are customizable, POSS additives can achieve greater compatibility with the polymer matrix and yield composites with superior mechanical properties.[62-64] Pan and Qiu[64] found that OctaIsobutyl-POSS dispersed well in poly(L-lactide) and that the storage modulus of the nanocomposite significantly increased from that of neat polymer. They also

reported that the crystallization time at 128 °C of the nanocomposite was shortened to 21 min. And, most recently, POSS has been used to improve the flammability of intumescent poly(lactic acid) composites while also increasing stiffness and tensile strength.[57]

We have recently reported on the synthesis of POSS-modified cellulose[65] and cellulose encapsulated POSS.[66] Investigation of the thermal and burning properties of flame-retarded PLA containing APP and POSS-modified cellulose reveal an improvement in storage modulus and reduction in hydrolytic degradation while maintaining a V-0 flammability rating and reduced heat release rate when compared to conventional IFRs.[48, 67] In the current work, PLA was melt-blended with each component of an intumescent flame retardant formulation to systematically analyze the effects of each component on the flammability, crystallinity, viscoelastic, and tensile strength properties of the composites. Samples were characterized with gel permeation chromatography, differential scanning calorimetry, powder X-ray diffraction, and melt rheology.

2. Experimental*

2.1. Materials

Toluene (Acros, 99%), ethyl alcohol (Aaper, USP 200), chloroform (Fisher Scientific, ACS grade, < 1% ethanol stabilized), NaOH (Fisher, ACS grade), acetic acid (Aldrich, 99.8%), OctaPhenylPOSS (Hybrid Plastics), and GlycidylPhenylPOSS (Hybrid Plastics) were used as received. De-ionized water (> 16 MΩ) was obtained from a Barnsted E-pure 3-module water purification system. Nanofibrillated cellulose (NFC, L040-6 grade, prepared by fibrillating the ends of 6 mm lengths of Lyocell regenerated fibers until reaching an MSR drainage of 40 mls), was obtained from Engineered Fibers Technology. The nanofibrils had an average diameter between 50 nm and 100 nm. The received fibers contained some impurities, which were removed with consecutive washes in 1 M acetic acid, deionized water, and 50/50 (v:v) ethanol/water

* The policy of NIST is to use metric units of measurement in all its publications, and to provide statements of uncertainty for all original measurements. In this document however, data from organizations outside NIST are shown, which may include measurements in non-metric units or measurements without uncertainty statements.

solutions. The fibers were then dried at 90 °C for 24 h and partially de-bundled manually prior to use. Ammonium polyphosphate (APP, Clariant EXOLIT AP422 (NH₄PO₃)₁₀₀₀₊), pentaerythritol (PER, Avacado, > 98%), & poly(lactic acid) (PLA, NatureWorks, PLA2002D) were dried for 1 h at 90 °C in a convection oven prior to use. POSS-modified cellulose using a 2:3 mass ratio of POSS to cellulose was prepared in toluene as described previously.[65]

2.2. Preparation of Poly(lactic acid) Composites

PLA composites were prepared by melt blending at 180 °C and 21 rad/s for 5 min in an Xplore 15 mL twin-screw co-rotating mini-compounder (DSM Instruments). Components were dried at 90 °C for 1 hr prior to charging the extruder. The abbreviations for the prepared composites are provided in Table 1.

Table 1. Abbreviations used for polymers and composites described in this manuscript.

Abbreviation	Composite Formulation
PLA	PLA2002D, as received
PLA-E	PLA2002D, extruded
PLA-APP	PLA2002D, extruded with 11.25% APP (by mass)
PLA-PNFC	PLA2002D, extruded with 3.75% PNFC (by mass)
PLA-NFC	PLA2002D, extruded with 3.75% NFC (by mass)
PLA-PER	PLA2002D, extruded with 3.75% PER (by mass)
PLA-Ph8POSS	PLA2002D, extruded with 3.75% OctaPhenyl POSS (by mass)
PLA-APP/PNFC	PLA2002D, extruded with 11.25% APP and 3.75% PNFC (by mass)
PLA-APP/NFC	PLA2002D, extruded with 11.25% APP and 3.75% NFC (by mass)
PLA-APP/PER	PLA2002D, extruded with 11.25% APP and 3.75% PER (by mass)

2.3. Instrumentation

PLA or PLA composites were dissolved in a small amount of chloroform and filtered through a 0.2 µm PTFE filter disc using a glass syringe. The filtered PLA was cast in a glass dish, air dried, then placed in an oven at 90 °C until the mass did not change. If necessary, the filtering was

repeated to form thin, transparent, colorless films. The molecular weight distributions of the PLA films were analyzed using Gel Permeation Chromatography (GPC) by Polymer Standards Service. Films were dissolved in chloroform to form 5.0 g/L solutions and injected into a PSS GPC system using an autoinjector with 100 μ L injection volume. The GPC system consisted of a PSS SDV precolumn (5 μ m, 100 \AA , ID 8.0 mm \times 50 mm), 3 size distribution columns (5 μ m, 100 \AA , ID 8.0 mm \times 300 mm; 5 μ m, 1000 \AA , ID 8.0 mm \times 300 mm; and 5 μ m, 1×10^5 \AA , ID 8.0 mm \times 300 mm), a PSS SECcurity 1200 HPLC pump, and a PSS SECcurity 1260 differential refractometer (RID). Calculations were performed using 15 polystyrene standards (370 Da to 2.52 MDa) and PSS WinGPC UniChrom, version 8.1 software. Data collected from all samples is believed to have an error of ± 5 %.

Horizontal and vertical burn tests were conducted in a fume hood using UL-94 standard procedures. Composite samples were hot pressed (25 MPa) into 125 mm \times 13 mm \times 3 mm molds at a temperature of 170 $^{\circ}$ C using a Carver hydraulic heated press. The reported burn rates have an uncertainty of $\sigma = \pm 0.2$ mm/min.

Powder x-ray diffraction experiments were performed on a Rigaku Miniflex II powder x-ray diffractometer. The d-spacing was calculated from peak positions using Cu K α radiation ($\lambda = 0.15418$ nm) and Bragg's Law. Samples were prepared by pressing (6 atm) 0.5 g in a hydraulic press at 170 $^{\circ}$ C. Standard x-ray measurements were performed over a 2θ range of 2 $^{\circ}$ –40 $^{\circ}$ at a scan rate of 0.5 $^{\circ}$ /min with an uncertainty of $2\sigma = \pm 0.001^{\circ}$. Spectra were deconvoluted and percent crystallinities were calculated using the PDXL integrated powder x-ray diffraction software.

Thermal properties of poly(lactic acid) composites were characterized using a TA Instruments Q-2000 Differential Scanning Calorimeter connected to a Refrigerated Cooling System. 3.0 mg \pm 0.2 mg samples were placed in aluminum pans with unsealed lids and the cell was purged with nitrogen at a flow rate of 50 mL/min. The samples were heated to 170 $^{\circ}$ C at a scan rate of 40 $^{\circ}$ C/min and held at 170 $^{\circ}$ C for 5 min to melt the composites and erase thermal history. Then, samples were cooled to 20 $^{\circ}$ C (below the glass transition temperature) and heated to 90 $^{\circ}$ C for crystallization at 40 $^{\circ}$ C/min. The samples were annealed at 90 $^{\circ}$ C for 30 minutes, then quenched

to 20 °C at a cooling rate of 40 °C/min. Samples were then heated to 170 °C at 10 °C/min for data collection. Each composite was analyzed in triplicate. The uncertainties are $\sigma = \pm 0.4$ °C for the reported temperatures and $\sigma = \pm 0.3$ J/g for the heat flow.

Dynamic rheological experiments were performed on a TA Instruments AR-G2 oscillatory rheometer using 25 mm parallel plate geometry. Samples used for rheological experiments were disks of 23 mm diameter and ca. 2 mm prepared from compression molding. Rheological experiments were conducted in an inert nitrogen atmosphere at 170 °C, 180 °C and 190 °C for each specimen. Isothermal tests were performed with a frequency sweep between 0.1 rad/s and 100 rad/s and a strain amplitude of 5 %. This strain amplitude was ascertained to be within the linear viscoelastic region of all the samples. Care was also taken to ensure that the normal force measured by the instrument was negligible prior to beginning each rheological experiment.

The specimens for tensile tests (type 1BA, EN ISO 527- 2) of 1.5 mm thickness were produced by injection molding using a DSM mini-injection molding machine (3.5 cm³, cylinder capacity). The granules were dried before injection molding (overnight at 60 °C, under vacuum). The temperature for injection molding was 190 °C, whereas the mold temperature was fixed at 70 °C. Due to a higher viscosity of the melt, a slightly higher injection molding temperature of 195 °C was necessary for the composites: PLA-E and PLA-PNFC. Tensile tests were performed using a Lloyd LR 10K tensile bench in accordance with the ASTM D 638-02a norm at a speed rate of 1 mm/min and using a distance of 58 mm between grips. All tests were carried out on specimens previously conditioned for at least 48 hours at 20 (± 2) °C under a relative humidity of 50 (± 3) % and the values were averaged over a minimum of five measurements for each sample.

3. Results and Discussion

3.1. Structural & Interfacial Properties

Differences in viscoelastic behavior of the composites were initially observed during the melt-mixing process. Forces exerted in the extruder during processing increased when blending fibers and decreased when adding ammonium polyphosphate (APP) or pentaerythritol (PER). Similar

to previous observations,[17] the color of the extruded composites revealed relative levels of degradation. Figure 1 illustrates the effects of each additive on the extruded and hot pressed composites. The addition of fibers or PER led to opaque composites, suggesting the formation of microcomposites. In addition, the PLA-PER composites cracked while cooling in the compression mold, illustrating a large decrease in impact strength. The addition of APP resulted in black composites, indicating acidic degradation of PLA and potentially some crosslinking. Combining APP and POSS-modified cellulose (PNFC) resulted in dark brown composites, whereas combining APP and nanofibrillated cellulose (NFC) or APP and PER produced composites with a resultant color consistent with simple combination of the two additives. This suggests that PNFC has the ability to inhibit the degradation processes during extrusion.

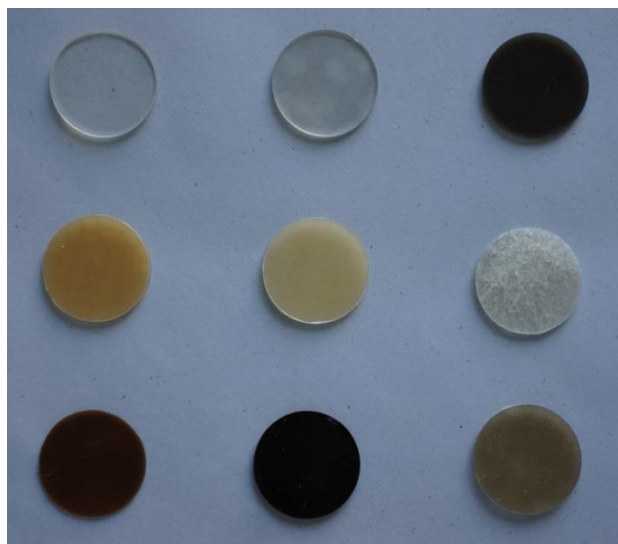


Figure 1: Colors of extruded and melt pressed composites. From left to right, top to bottom, the composites shown are PLA, PLA-E, PLA-APP, PLA-PNFC, PLA-NFC, PLA-PER, PLA-APP/PNFC, PLA-APP/NFC, and PLA-APP/PER.

The physical characteristics observed during extrusion indicate varying degrees of degradation depending on the additive used. The molar mass of the extruded composites were characterized by gel permeation chromatography and are shown in Table 2. As observed by others, the PLA degrades while in the molten state,[10, 68, 69] resulting in a 15 % loss in molar mass in this study. Addition of APP further degrades the polymer, likely due to the formation of poly(phosphoric acid). It has been suggested that PLA degrades at its slowest rate at about pH =

5.0,[70] and the pure PLA melt used in this study was found to have a pH between 4.0 and 4.7 using acid-base dyes.[71] PER appears to degrade PLA as much as APP and is additive when combined with APP, though the exact cause is not known. Fibers do not appear to affect the degradation, whether added alone or in combination with APP. The one exception is the combination of APP and PNFC, which reduces the degradation of PLA relative to the addition of APP alone. This is in agreement with the viscosity average molar mass trend observed in PLA composites with 5 % flame retardant additives.[17] The polymer dispersion index remained unchanged for all composites, indicating that the composites are fairly well dispersed on the micro-scale and that the degradation occurs randomly and indiscriminately of polymer size.

Table 2: Molar Mass of filtered composites by GPC.

Sample	M _n (kDa)	M _w (kDa)	M _z (kDa)	M _p (kDa)	PDI
PLA	55.8	116	200	95.3	2.08
PLA-E	45.6	96.4	162	81.2	2.11
PLA-PNFC	45.1	93.4	160	78.5	2.07
PLA-NFC	33.5	92.0	162	79.8	2.74
PLA-PER	37.5	79.6	142	69.2	2.12
PLA-APP	34.7	74.4	123	65.6	2.14
PLA-APP/PNFC	39.8	89.4	151	78.3	2.25
PLA-APP/NFC	36.8	78.5	140	67.7	2.13
PLA-APP/PER	33.0	68.1	115	59.7	2.06

Note: M_n = number average, M_w = weight average, M_z = z-average, M_p = peak, PDI = polydisperse index (M_w/M_n). Polymer samples were dissolved in CHCl₃ for both filtering & GPC.

3.3. Flammability Properties

The flammability properties of the composites were characterized by UL-94 horizontal and vertical burn tests, as shown in Table 3. The horizontal burning characterization of PLA are quite variable test to test, but were not significantly affected by extrusion. The unextruded PLA extinguished twice prior to the 25 mm mark, once 5 mm after the mark, and once 20 mm after

the mark. The burn rate was about the same for all samples. PLA-E extinguished twice prior to the 25 mm mark, once 5 mm after the mark, and once 8 mm after the mark. The burn rate was about the same as the unextruded PLA for all four tests. The addition of cellulose slightly increased the burn rate and resulted in complete consumption of the test bars. Both PNFC and PER reduced the flammability of the composite, though both composites failed the vertical burn tests. PLA-PNFC did appear to be slightly more flammable than PLA-PER, as the flame extinguished 1 – 2 seconds after removal of the Bunsen burner for PNFC versus 0 – 1 seconds for PER. It was observed that the elongation of the composite while burning PLA-PER was much higher than in any other composite, which may have cooled the material due to increased surface area. In the PLA-PNFC composite, the melt appeared to have lower cohesion than other composites, with larger burning drips that included some unmelted material. This may have been due to an increase in viscosity of the melt with the addition of the fibers. The addition of APP produced composites that extinguished in the vertical burn test as soon as the Bunsen burner was removed, but still generated burning drips during the ignition. Similar to what has been reported by Bourbigot and others, this resulted in a composite with a V-2 rating.[6] The addition of APP with any carbon source resulted in composites with nonflaming drips during ignition and flames that extinguished less than 1 s after removing the ignition source, as previously reported.[67]

Table 3. UL-94 burn test results of poly(lactic acid) composites

Composite	HB rate (mm/min)	HB length (mm)	VB t ₁ (s)	VB t ₂ (s)	UL-94
PLA	9.4	20	complete		NR
PLA-E	9.2	8	complete		NR
PLA-PNFC		0	complete		HB
PLA-NFC	9.9	75	complete		NR
PLA-PER		0	complete		HB
PLA-APP		0	DNB	DNB	V-2
PLA-APP/PNFC		0	DNB	DNB	V-0
PLA-APP/NFC		0	DNB	DNB	V-0
PLA-APP/PER		0	DNB	DNB	V-0

3.4. Crystallinity

Crystalline phases of the composites were examined using powder x-ray diffraction (XRD) after quench cooling samples and after annealing at 90 °C for 30 minutes. (cf Figure 2) In the quenched composites, there were no visible crystalline peaks associated with poly(lactic acid). Two amorphous peaks were evident, which could be convoluted using the PDXL integrated XRD software. A very small peak at 21.55° in the cellulose-containing samples was assigned to cellulose II. The two largest peaks associated with APP at 14.90° and 15.75° did not interfere with any other crystalline peaks. The peaks associated with PER all had interferences with other crystalline phases. In the annealed composites, peaks associated with crystalline PLA appeared. The two largest crystalline peaks for PLA at 16.60° and 18.90° did not interfere with any peaks associated with the other additives. In the pristine PLA sample the percent crystallinity was calculated to be 0.56%, which increased to 17.1% for the extruded sample. This is consistent with previous reported results regarding the increased crystallinity of PLA after extrusion.[72] The samples containing APP all had the same quantities of APP in them, so comparison of the ratio, $A_{15.75}/A_{16.60}$ could be used to determine relative crystallinities of PLA in the intumescent composites. The crystallinity was found to increase in the order, PLA-APP < PLA-APP/PER < PLA-APP/PNFC < PLA-APP/NFC.

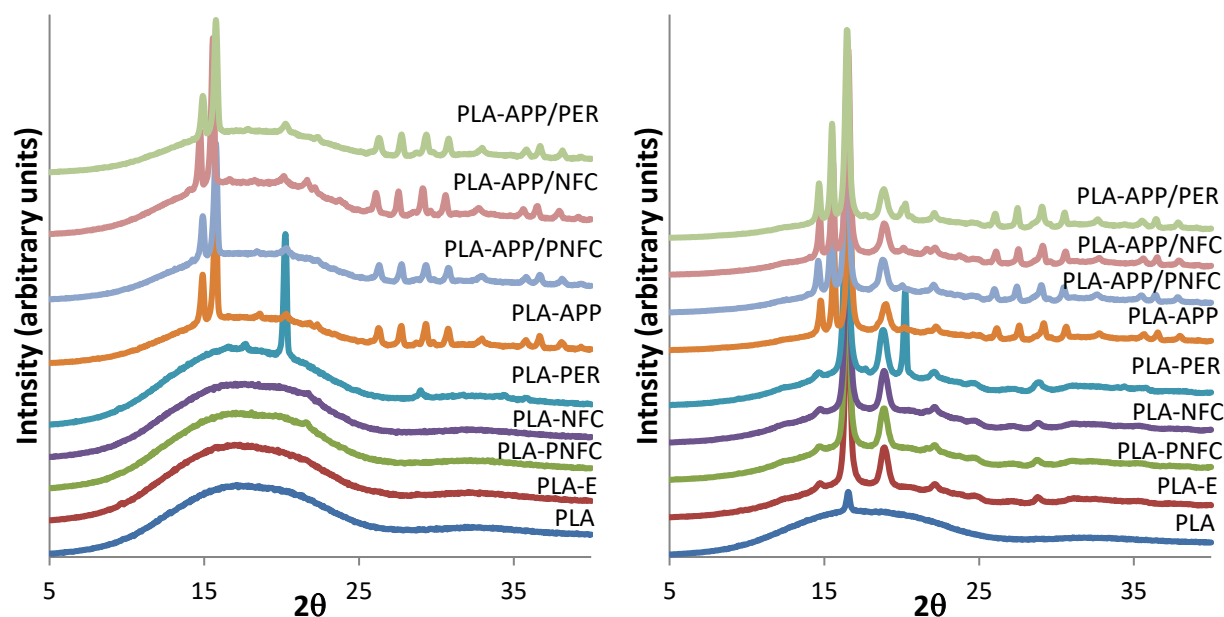


Figure 2. Powder x-ray diffraction of PLA composites containing intumescent flame retardants (a) quenched after compression molding and (b) after annealing at 90°C for 30 min. Plots have been shifted vertically for clarity.

Differential scanning calorimetry was used to assess the transition temperatures of the composites after annealing. The PLA used in this study exhibits a double-melting peak (cf Figure 3), which has been attributed to the formation of imperfect small crystals at lower temperatures followed by melting and recrystallization of larger, more perfect crystals at higher temperatures.[73-76] Factors that contribute to higher order, including longer curing times, higher optical purity, and nucleating agents, result in larger second melting peaks at higher temperatures. The transition temperatures for the composites obtained from DSC are shown in Table 4. The reported heat of fusion values are in J/g of composite, but the percent crystallinity has been adjusted to reflect J/g of poly(lactic acid). PLA2002D is a high molecular weight poly(l-lactic acid), with a 4 % by mass d-lactic acid content, leading to very slow crystallization kinetics. The 30 minute annealing time used in the DSC scans was only sufficient enough to crystallize 1% of the PLA, similar to what was observed in XRD. The degradation of PLA that occurs during extrusion increases the crystallization rate, leading to an average crystallinity of 26% after the 30 minute annealing. This suggests that the 30 minute annealing time was insufficient to complete the crystallization process for the larger XRD samples shown previously. The slight increase in glass transition temperature may be due to the loss of residual monomer. (PLA2002D from the manufacturer typically contains about 0.3 % by mass residual

monomer). The additives have only minor effects on the transition temperatures, but they significantly alter the crystallinity of the PLA. The glass transition is broadened, suggesting some entanglement between the additives and the PLA matrix. The presence of cellulosic fibers or POSS does not significantly alter the transition temperatures or the crystallinity. Mathew, Oksman, and Sain also observed that cellulose acts as a nucleating agent, increasing the crystallinity of pristine PLA while attaining the same total crystallinity as PLA when annealed.[77] However, the presence of POSS appears to inhibit the formation of the more perfect crystals while maintaining the total crystallinity of the PLA. The presence of APP increases the glass transition, lowers the melting point of the imperfect crystals slightly, and markedly increases the crystallinity of PLA, regardless of the addition of a carbon source. The APP used in this study has a molar mass of about 90 kDa. The observed increase in glass transition of the PLA composite is likely due to polymer entanglement, inhibiting the segmental motion of PLA. PER acts as both a nucleating agent and as a plasticizer, and more of the lower temperature PLA crystals are formed. The increase in crystallinity when adding APP and PER may be one of the factors leading to increased brittleness when these flame retardants are used.[42, 44] The crystallinity increase can be moderated slightly by using cellulose fibers, particularly PNFC, as the carbon source. This is in contrast with the XRD data, which show higher crystallinities for PLA-NFC and PLA-PNFC. It may be that the larger samples used in x-ray studies may not have been annealed long enough for complete crystallization. This would be consistent with the lower crystallinity found in the annealed PLA-E XRD sample and with the increased crystallization rate in the presence of cellulose noted in previous crystallization[13, 77] and dynamic mechanical analysis results.[17]

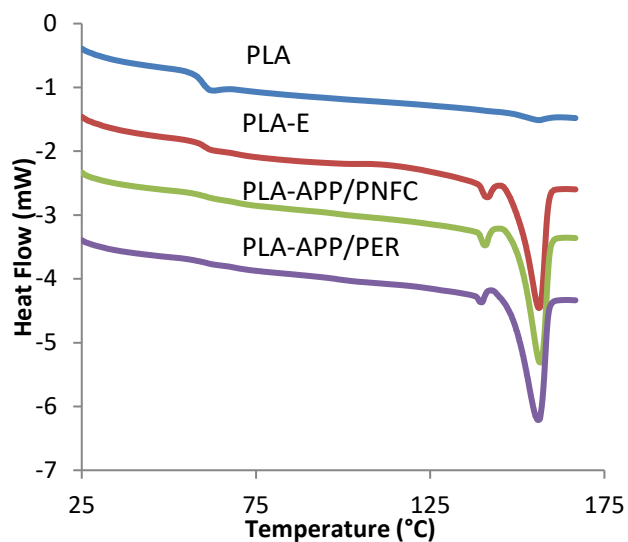


Figure 3. Sample DSC scan of annealed PLA, PLA-E, PLA-APP/PNFC, and PLA-APP/PER, depicting a glass transition and two melting peaks. Plots have been shifted vertically for clarity.

Table 4: Thermal properties of annealed composites by DSC.

Sample	T_g (°C)	T_1 (°C)	T_2 (°C)	ΔH_1 (J/g)	ΔH_2 (J/g)	% Cryst.
PLA	60.0	---	156.2	0	0.89	0.95
PLA-E	60.8	141.6	156.3	1.36	22.7	25.7
PLA-PNFC	60.8	141.3	155.7	1.70	22.6	27.0
PLA-NFC	60.4	141.4	155.9	1.42	22.3	26.4
PLA-PER	59.4	140.1	155.6	1.41	28.3	33.0
PLA-APP	61.6	140.7	156.6	1.59	25.5	32.7
PLA-Ph8POSS	60.9	141.6	155.0	1.44	21.6	25.6
PLA-APP/PNFC	61.7	140.7	156.5	1.45	23.6	31.4
PLA-APP/NFC	61.7	140.8	156.5	1.22	24.4	32.2
PLA-APP/PER	61.2	140.5	156.1	0.80	26.8	34.7

% Crystallinity determined using ΔH_{fus} , where 100% crystalline PLA = 93.5 J/g.

3.5. Melt Viscosity Behavior

The processability of the composites was assessed by examining the oscillatory rheology of the melt at temperatures below the decomposition of the IFR. Complex viscosities for the composites at 170 °C are shown in Figure 4. PLA is known to exhibit shear thinning behavior,[78] which was observed at frequencies higher than 10 rad/s for pure PLA. The decrease in viscosity after extrusion is due predominantly to the decrease in molar mass.[78-80] The viscosity decreased slightly in the order PLA > PLA-APP > PLA-NFC. This was somewhat surprising, as the cellulosic fibers were expected to increase viscosity[81, 82] and the APP was expected to decrease viscosity due to the large decrease in PLA molar mass. This suggests that the cellulose was not well dispersed and that APP has good interfacial adhesion with PLA, resulting in polymer chain entanglement. The combination of APP and NFC did result in the expected rise in viscosity. All of these composites exhibited similar shear thinning behavior over the frequency range studied. The addition of PER or PNFC, however, exhibited a plasticizing effect with a much larger decrease in viscosity at low shear rates. Since PLA-APP/PER contains the plasticizing PER and has the lowest molar mass, it has the lowest viscosity of all the composites. When incorporated into a polymer matrix, POSS can reduce polymer motion through steric hindrance (leading to higher T_g and higher viscosity at low shear) or it can plasticize polymer motion due to its large void volume (leading to lower T_g and lower viscosity at low shear). In PNFC, the bulkiness of POSS appears to dominate, suggesting poor miscibility with PLA. However, in PLA-APP/PNFC, there is a very large viscosity at low frequencies, followed by a steady decrease at high frequencies. This is due to the cross-linking between cellulose and PLA through the opened cage structures on some of the POSS molecules.[17] At low shear, there is a large entanglement, which is disrupted at high shear, allowing the plasticizing effect of the POSS substituents. The temperature dependence of the complex viscosity, shown in Figure 5, supports this hypothesis, since the viscosity decrease with temperature is much smaller at low frequencies than at high frequencies.

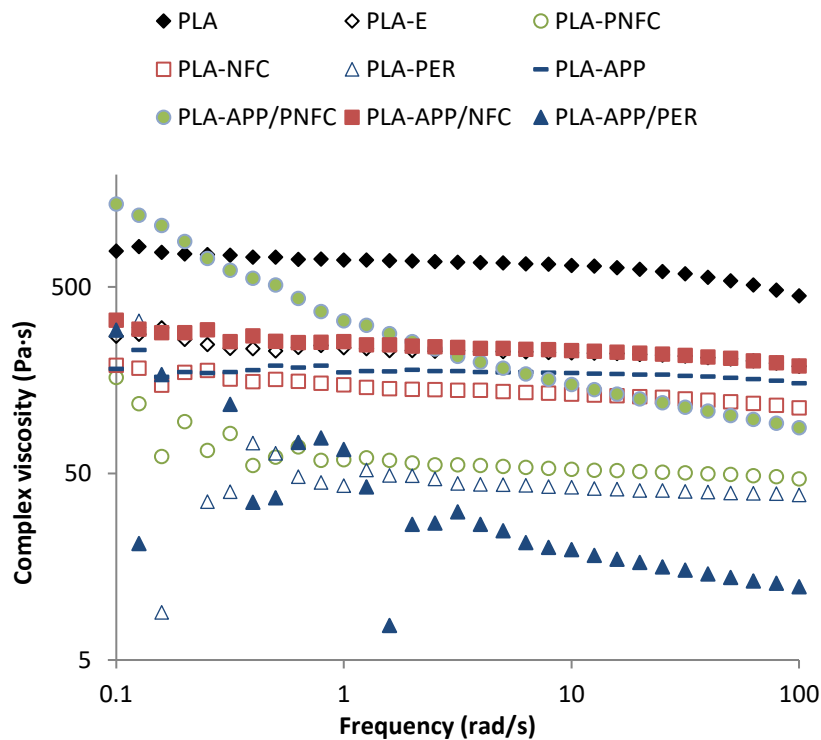


Figure 4. Complex viscosity of PLA composites at 5% strain vs. shear rates at 170 °C.

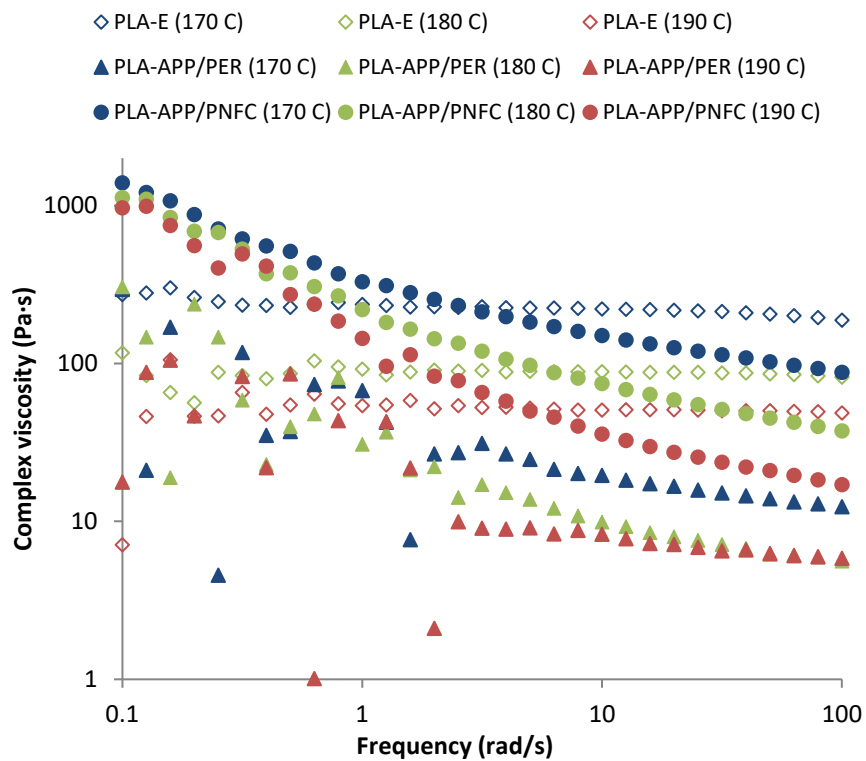


Figure 5. Temperature dependence of complex viscosity of PLA-E, PLA-APP/PNFC, and PLA-APP/PER at 5% strain.

The storage modulus and loss modulus of the composites at 170 °C is shown in figure 6. All composites except PLA-APP/PER and PLA-APP/PNFC exhibit similar profiles over the entire frequency range. The storage modulus increases at slightly faster rates as the frequency increases while the loss modulus increases linearly at a faster rate. The $\tan \delta$ (not shown) exhibits a maximum around 1 rad/s for all of these composites. The storage modulus and loss modulus increase at much lower rates for PLA-APP/PER and PLA-APP/PNFC, and their behavior over the frequency range are very similar. The estimated zero storage modulus for PLA-APP/PER is an order of magnitude higher than all the other composites, indicating a more solid-like behavior. The $\tan \delta$ for these two composites is nearly linear over the frequency range.

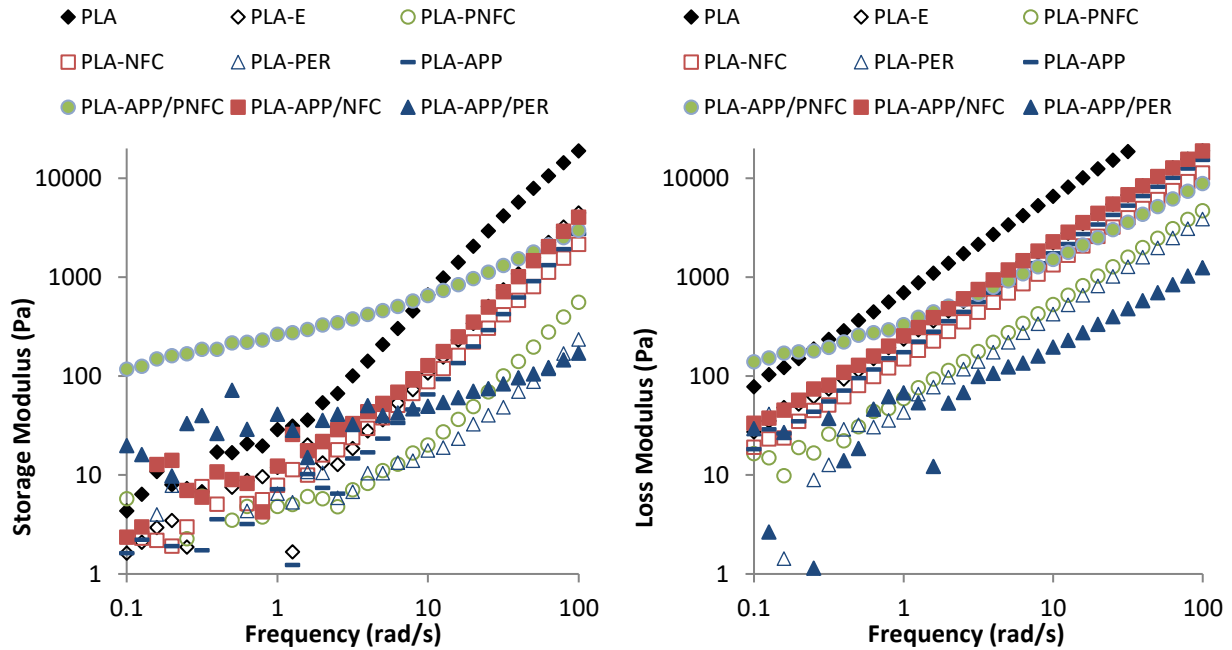


Figure 6. (a) Storage modulus and (b) loss modulus of PLA composites at 5% strain vs. shear rates at 170 °C.

3.6. Tensile Strength

The tensile strengths of the composites are shown in Table 5, and an image of the specimens after testing are shown in Figure 7. The addition of POSS-modified cellulose may have lowered all the tensile properties slightly, but the deviations from pure extruded PLA was within the

experimental error. Since short cellulosic fibers typically reduce the tensile strength of undrawn PLA,[13, 83] it is likely that the surface coverage of POSS is sufficient enough in PNFC to maintain polymer strength. The addition of APP did not affect Young's modulus, but did significantly reduce the strain at yield and break and slightly reduced the elongation at yield. The elongation at break appeared unaffected. It has been previously observed that APP, and intumescent formulations in general, reduce the tensile properties of the composite compared to the pristine polymer matrix.[40, 42-44, 49] The slight loss in elasticity for PLA-APP/PER is due to the plasticizing effect of PER and is consistent with the dynamic mechanical analysis results previously reported.[48, 67] The trends in the yield strength and elongation appear to correlate with the molar mass of the PLA. The elongation at break increased only for the PLA-APP/NFC. This is likely due to the presence of longer cellulose fibers,[84, 85] which may reduced in size for PNFC due to the partial dissolution and regeneration during the alkali synthesis process. The use of PER as a carbon source produced composites with the largest decrease in tensile strength, whereas the use of PNFC produced composites with the smallest drop in tensile strength.

Table 5. Comparative mechanical properties of flame retarded PLA composites

Sample code	E (MPa)	σ_y (MPa)	σ_b (MPa)	ϵ_y * (%)	ϵ_b * (%)
PLA-E	3380 (± 100)	64 (± 1)	63 (± 1)	2.9 (± 0.1)	3.0 (± 0.1)
PLA-PNFC	3280 (± 170)	63 (± 1)	62 (± 1)	2.8 (± 0.1)	2.9 (± 0.1)
PLA-APP/PNFC	3240 (± 90)	49 (± 1)	42 (± 4)	2.6 (± 0.2)	3.1 (± 0.4)
PLA-APP/NFC	3400 (± 260)	49 (± 1)	37 (± 2)	2.6 (± 0.1)	4.6 (± 0.6)
PLA-APP/PER	2940 (± 150)	45 (± 1)	43 (± 2)	2.2 (± 0.1)	2.6 (± 0.4)

* ϵ_y = nominal strain at yield; ϵ_b = nominal strain at break.
Standard deviations are given in brackets.

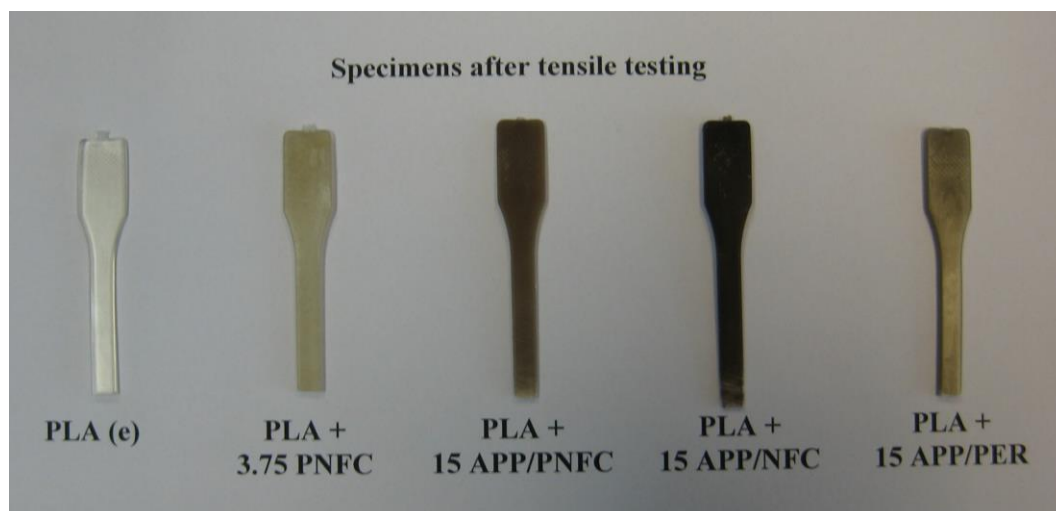


Figure 7. Images of specimens after tensile testing.

4. Conclusions

POSS-modified cellulose nanofibers (PNFC) form a cross-linked structure when melt-blended with PLA. This structure helps form an integrated network and protects the composite from acid hydrolysis during extrusion, which minimizes both cellulose and PLA degradation. It was verified that both components of the conventional intumescent flame retardant, ammonium polyphosphate (APP) and pentaerythritol (PER) catalyze the degradation of PLA during extrusion. The addition of unmodified cellulose (NFC) increases the flammability of PLA, even at the low loading of 3.75 % by mass. Use of the POSS-modified cellulose improves flammability to achieve an HB rating in UL-94 tests. The addition of only APP produces a composite with a V-2 rating. Further addition of cellulose or PER achieves a V-0 rating. The addition of cellulose increased the crystallization rate of PLA, but did not affect the total crystallinity. Both APP and PER increase the crystallinity of PLA. Furthermore, PER was found to have a plasticizing effect on the polymer. PNFC had the ability to limit the crystallinity increase of APP additions. The melt viscosity behaviors of the composites were very similar to each other, with the exception of PLA-APP/PNFC and PLA-APP/PER. For the intumescent composites, complex viscosities indicated competing factors of PLA degradation (lower viscosities) and polymer entanglements with APP (higher viscosities). Both PER had a plasticizing effect, which dominated the melt rheology behavior of composites containing this

component. PNFC also had a plasticizing effect, but the cross-linked network that formed in the presence of APP dominated its rheological behavior. Viscosity and storage modulus were high at low shear and did not decrease much with increasing temperature. At high shear, the network was disrupted, and the plasticizing effect of PNFC dominated. Tensile tests indicated that Young's modulus was relatively invariant with any additive, though a small decrease was observed for the PLA-APP/PER composite. The tensile strength and elongation decreased by 25 % and 10 %, respectively, when adding APP with any carbon source. The addition of only PNFC did not affect the tensile properties. PLA-APP/PNFC exhibited the best tensile properties among all the intumescent PLA composites. The ability of PNFC to form a cross-linked network with APP reveals the benefits of using this carbon source for flame retarding PLA.

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